Functionalised Polythiophenes: Synthesis, Characterisation and Applications

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Functionalised Polythiophenes: Synthesis, Characterisation and Applications

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Abstract

Conducting polymers display properties such as high conductivity, light weight and redox activity giving them great potential for use in many applications. Polythiophenes have proved to be particularly useful because they are readily functionalised and have good chemical stability. The purpose of this work was to investigate the effect of electron-withdrawing and electron-donating substituents on the synthesis and properties of polythiophenes.

Initial work entailed the synthesis of a series of styryl-substituted terthiophenes. Polymerisation of these materials using both chemical and electrochemical methods was found to produce predominantly short chain oligomers (n < 4) and insoluble material that could not be further processed.

An analogous series of styryl-substituted terthienylenevinylene materials were electrochemically oxidised for comparison to the terthiophene series. These materials were also found to produce predominantly dimer and short oligomers, but with the expected higher conjugation length than the corresponding terthiophene oligomers.

To enhance polymerisation and increase the solubility of the resulting materials, the polymerisation of styryl-terthiophenes with alkyl and alkoxy functionalities was investigated. The properties of the resulting polymeric materials were determined using electrochemistry, mass spectrometry, spectroscopy and microscopy. The alkoxy substituted polymer was found to have a longer average polymer length than the corresponding alkyl derivative (~n = 11 compared to ~n = 6), but was less soluble (78% compared to 100%). It was found, however, that by increasing the alkoxy chain length from 6 carbons to 10 carbons, the solubility of the polymer could be increased to 97% without affecting the average polymer length. The alkoxy-substituted polymers were observed to be very stable in the oxidised, conducting state compared to the alkyl-substituted polymer, which appeared to be more stable in the neutral, non-conducting state. It was found that these soluble materials could be separated into

fractions of different length polymers by using sequential soxhlet extractions in different solvents.

Preliminary investigations were made into the suitability of these soluble oligomeric and polymeric materials for use in photovoltaic, actuator and organic battery applications and promising results were achieved for actuator and battery functions. In addition, the solubility of these materials allowed nano- and micro-structured fibre and fibril surfaces to be prepared for use in high surface area electrodes.

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CHAPTER 7

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List of Symbols

A	Ampere
A	Ammeter
A^-	Anion
b	Variable number
δI_E	Photovoltaic activity
δI_{SC}	Photovoltaic activity under short circuit
E	Potential
E^0	Standard electrode potential
e^-	Electron
EE	Electrochemical efficiency
EE_{ox}	Electrochemical efficiency on oxidation
EE_{red}	Electrochemical efficiency on reduction
E_{K}	Kinetic energy
E_{ox}	Peak oxidation potential
$E_{\mathrm{oxidation\ onset}}$	Oxidation onset potential
E_{red}	Peak reduction potential
F	Faraday's constant
Fc	Ferrocene
H_H	Proton at head position (5-position)
H_T	Proton at tail position (5"-position)
$I_{\mathrm{dark},SC}$	Short circuit current, dark conditions
$I_{\mathrm{light},SC}$	Short circuit current produced under illumination
I_{pp}	Current at peak power
I_{SC}	Short circuit current (Current at zero potential)
λ_{max}	Wavelength at maximum absorbance in spectroscopy
m	Variable number
m	Mass
M	Molecular weight
M_{n}	Number average molecular weight

M_r	Molar mass
M_w	Weight average molecular weight
n	Oligomer length in terms of monomer units
n	Variable number
n	Number of electrons per monomer unit
N	Number of molecules
n_{av}	Average oligomer length in terms of monomer units
R	Variable functional group
R_f	Retention factor
t	Time
v	Velocity
V	Volt
V	Voltammeter
V_{OC}	Open circuit voltage (Potential at zero current)
V_{pp}	Voltage at peak power.
X^+	Variable cation
z	Charge

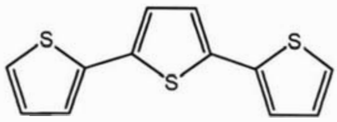
List of Abbreviations

ACTH	Adrenocorticotropic hormone
AFM	Atomic force microscopy
AN	Acetonitrile
Anhyd.	Anhydrous
CE	Counter electrode
CP	Conducting polymer
CV	Cyclic voltammetry
DBTT	3',4'-dibutyl-2,2':5'2"-terthiophene
DBU	1,8-diazabicyclo[5.4.0]undec-7-en
DCM	Dichloromethane
dppp	1,3-diphenylphosphinopropane
ECE	Energy conversion efficiency
EDG	Electron-donating group
EDOT	3,4-ethylenedioxythiophene
EE	Electrochemical efficiency
EI	Electrospray ionisation
EQCM	Electrochemical quartz crystal microbalance
Equiv.	Equivalents
EWG	Electron-withdrawing group
FAB	Fast atom bombardment
Fc	Ferrocene
FF	Fill factor
GPC	Gel permeation chromatography
GPES	General purpose electrochemical system
GRIM	Grignard method
HH	Head-to-head
HOMO	Highest occupied molecular orbital
Hrs	Hours
HT	Head-to-tail

ICP	Inherently conducting polymer
IPRI	Intelligent Polymer Research Institute
ITO	Indium tin oxide
LUMO	Lowest unoccupied molecular orbital
MALDI-TOF MS	Matrix assisted laser desorption/ionisation time-of-flight mass spectrometry
Me	Methyl
MCP	Micro-channel plate
N/A	Not applicable
NMR	Nuclear magnetic resonance
OFET	Organic field effect transistor
OLED	Organic light emitting diode
PCBM	3'-phenyl-3'H-cyclopropa[1,9][5,6]fullerene-C_{60}-I_h-3'-butanoic acid methyl ester
PD	Polydispersity
PEC	Photoelectrochemical cell
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEDOT-PSS	Poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate)
PEO	Polyethylene oxide
Ph	Phenyl
PMMA	Polymethylmethacrylate
PPV	Polyphenylenevinylene
PV	Photovoltaic
PVDF	Polyvinylidene fluoride
RE	Reference electrode
RT	Room temperature
SA	Surface area
SCE	Standard calomel electrode
SEM	Scanning electron microscopy
SHE	Standard hydrogen electrode
TBAP	Tetrabutylammonium perchlorate
$TBAPF_6$	Tetrabutylammonium hexafluorophosphate
TLC	Thin layer chromatography

THF	Tetrahydrofuran
TOF	Time-of-flight
TPP	Tetraphenyl porphyrin
TT	Tail-to-tail
UV-VIS-NIR	Ultraviolet-visible-near infrared
WE	Working electrode
w.r.t.	With respect to

Monomer Abbreviations



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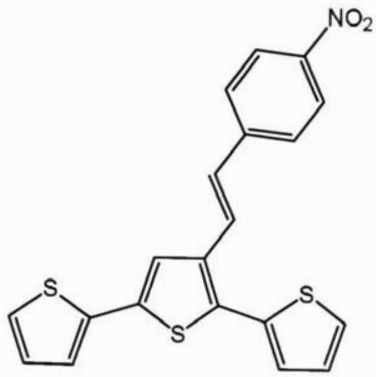

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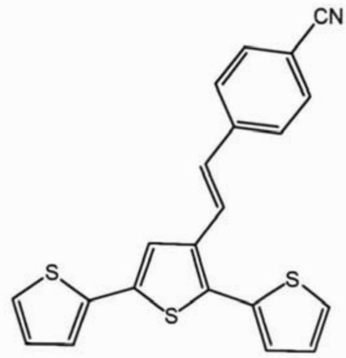

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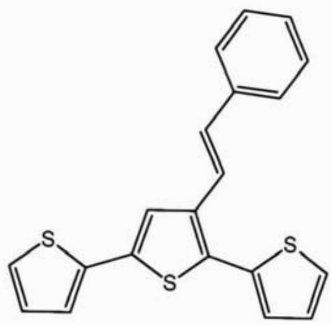

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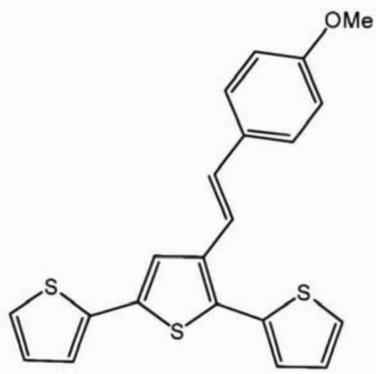

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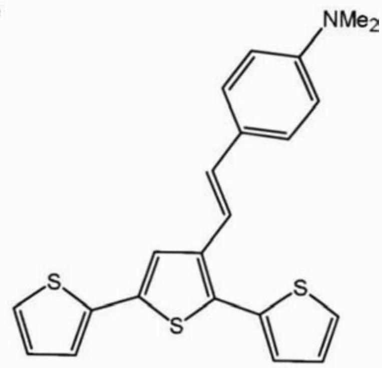

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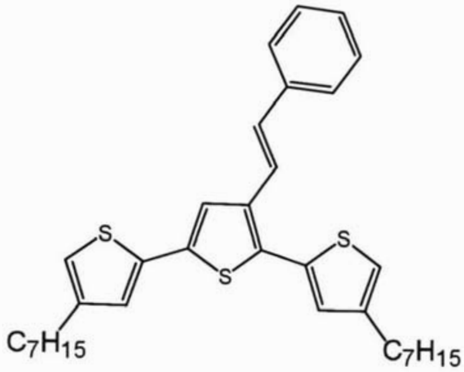

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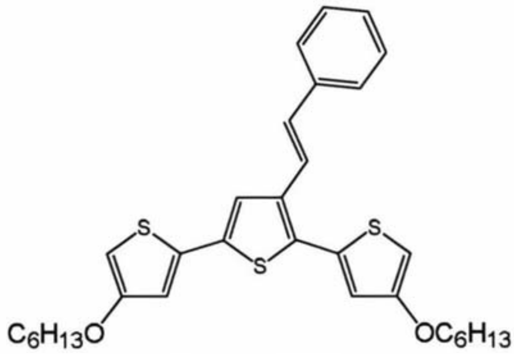

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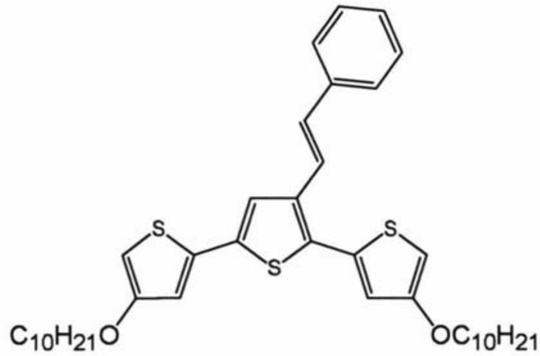

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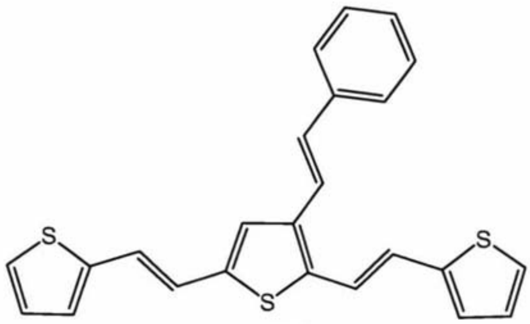

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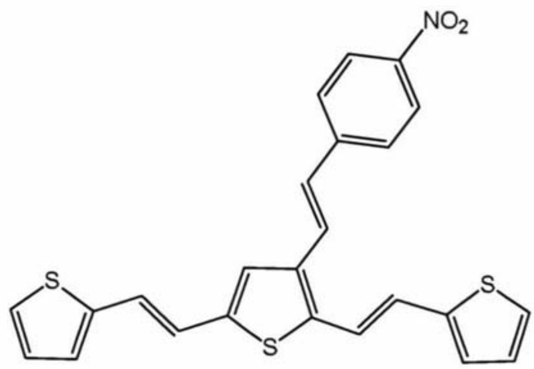

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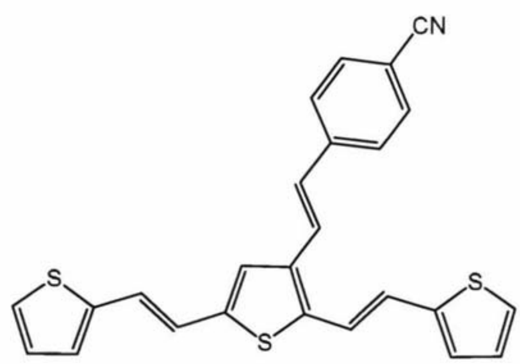

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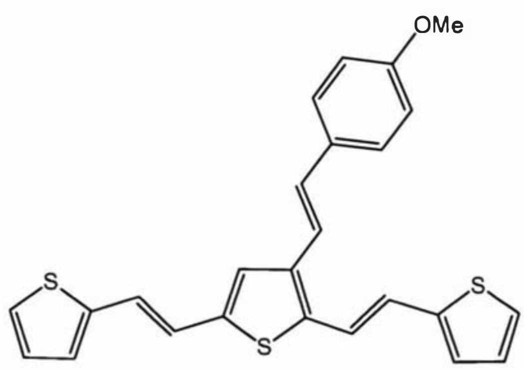

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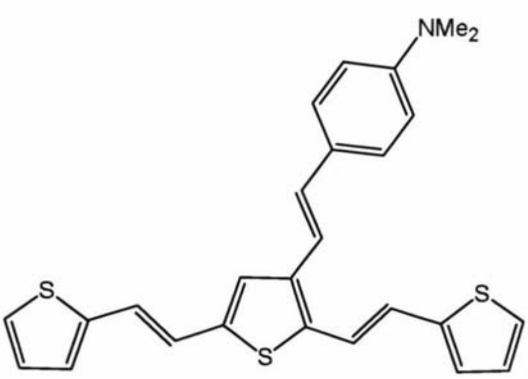

NMe_2STV

STT: Styryl terthiophene

DASTT: Dialkoxy styryl terthiophene or Dialkyl styryl terthiophene

STV: Styryl terthienylenevinylene